

Thin Si p-layers Containing Boron Doped Micro-crystalline Si and a-SiO_x Phases

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ABSTRACT

Thin films containing boron doped microcrystalline silicon were deposited by the standard RF PECVD system from a gas mixture of SiH₄, H₂, CO₂ for the purpose of developing a new type of p-layer for use in a-Si superstrate p-i-n solar cells. Films were characterized by Raman spectroscopy, SIMS analysis and in-plane conductivity measurements as a function of B₂H₆, H₂ and CO₂ input flows. Lower B₂H₆ flow increased the c-Si fraction. On SnO₂ substrates c-Si fraction increased with decreasing CO₂ and increasing H₂ flow. On glass substrates, the c-Si level increased with H₂ in the discharge but the CO₂ level did not have any effect. For 150Å thick films, c-Si was observed on glass but on SnO₂, a 10Å SiO_x base layer was necessary to obtain c-Si phase in the films.

Introduction

There has been considerable effort focused on changing the structure of the p-layer from amorphous to microcrystalline in order to improve the performance of a-Si:H based p-i-n solar cells. These μ c layers are typically inhomogeneous with a mix of a-Si or a-Si:C with c-Si crystallites of several tens of nanometers. The grain size, fraction crystallinity, and conductivity depend strongly on extrinsic variables such as the thickness and substrate and intrinsic variables such as H₂ dilution and power.

In a previous study we investigated the crystallinity of p-layers deposited from SiH₄ / CH₄ mixtures in a RF PECVD system and showed that films with controllable c-Si volume fraction can be obtained at low power densities [1].

In the present work we investigate RF PECVD deposition and subsequent characterization of microcrystalline p-layers having CO₂ in the feed gas. The goal was to obtain two phase films of crystalline Si imbedded in a matrix of a-SiO_x:H:C. The idea is that such films incorporated in p-i-n type devices could give high currents due to the transparency of the amorphous phase and high voltages due to the highly conductive crystalline phase with a smaller junction surface. Also, the presence of CO₂ in the glow discharge would tend to decrease the reducing effects of the plasma on the thin conductive oxides used as the front contact in superstrate devices.

Experimental

The p-layers were deposited on 7059 glass and on untextured SnO₂ coated soda lime glass substrates, and

their crystallinity and deposition rates were determined by Raman spectroscopy and by profilometry [1].

The main experimental variables were the hydrogen dilution and CO₂ content in the feed gases. The secondary parameters were discharge power density and doping gas (B₂H₆) level. In designing experiments and interpreting results normalized flows rather than the actual gas flows were used. These normalized flows were defined as, $o = f(\text{CO}_2) / [f(\text{SiH}_4) + f(\text{CO}_2)]$; $h = f(\text{H}_2) / [f(\text{SiH}_4) + f(\text{CO}_2)]$; $b = 2 \times f(\text{B}_2\text{H}_6) / [f(\text{SiH}_4) + f(\text{CO}_2)]$. Substrate temperature was 150°C. Partial pressures were kept constant by introducing He as a buffer gas.

Results

In a first step, we have performed a deposition under conditions that favor crystallinity and evaluated carbon and oxygen incorporation into the film. The conditions chosen were: $f(\text{SiH}_4) = 20$ sccm; Power Density = 420 mW/cm²; Pressure = 1 Torr; $h = 154$; $o = 0.23$; $b = 1.5 \times 10^{-3}$.

Raman spectra of the films show the existence of a two-phase mixture consisting of c-Si and amorphous silicon phases. Also, the film deposited on glass seems to have higher amounts of c-Si phase (45% vs. 35%).

SIMS depth profile of the films indicate that the composition of the films are independent of the substrate, and oxygen and carbon content in the films are respectively 10^{22} and 7×10^{20} .

It is important to note that since the films have a c-Si and an amorphous phase, the latter must contain almost all the hydrogen, carbon and oxygen observed in the SIMS analysis. Thus it can be concluded that the amorphous phase is essentially hydrogenated silicon oxide containing small amounts of carbon and boron.

Effect of Diborane Level in the Discharge

In the next step, films deposited at two different diborane dilutions $b=0.015$ and 0.0015 for a range of hydrogen dilution "h" were investigated for their crystallinity and deposition rates. Total pressure, silane partial pressure and discharge power density were respectively 5 mT, 1 Torr and 168 mW/cm².

It is found that for a diborane concentration of $b = 0.0015$, the onset of c-Si phase is observed at remarkably low hydrogen dilutions of $h = 23$ and 50 , respectively, for 7059 glass and tin oxide substrates, even at such a low power density utilized here.

More generally, it is found that the fraction of c-Si increases with increasing hydrogen dilution and decreases with increasing diborane level. However, the degree of

validity of this observation depends on the film deposition rates which are higher on SnO₂ substrates. This is because bonding rearrangement on the surface of the growing film that favors c-Si formation will be more extensive for low deposition rates. Consequently, dependence of crystallinity on hydrogen dilution is only valid in the regions where deposition rates do not change appreciably.

However the difference in crystallinity between glass and tin oxide substrates for a given diborane level might also be controlled, in addition to deposition rate, by the possible difference in the initial nucleation rate of crystallites on glass and tin oxide surfaces.

The difference in deposition rates between glass and SnO₂ substrates is most probably due to the voltage difference between the substrate and the plasma. In the case of a conductive substrate such as SnO₂ the surface is grounded and the potential difference between the substrate and the plasma is the plasma potential. In the case of a glass substrate, the potential difference is the floating potential which, in general, is the substantially smaller than the plasma potential.

Also observed was an increase in the deposition rate with a gas phase diborane concentration, which probably is related to the known ability of diborane in cracking silane molecules.

Effect of Hydrogen Dilution:

A number of films were deposited at different levels of hydrogen dilution for four different CO₂ levels, with $b = 1.5 \times 10^{-3}$, all other deposition parameters being the same. c-Si content in these films is given in Figure 1 for glass and SnO₂ substrates. The data show that while the CO₂ level in the discharge does not seem to have an effect on the c-Si content, in the case of glass substrates it does control crystallinity of the films deposited on SnO₂ substrates. Also as previously noted, increasing hydrogen dilution increases crystallinity and SnO₂ substrates give a lower c-Si fraction than glass substrates. The onset of crystallinity, as a function of hydrogen dilution is also different for the two substrate types being $h \leq 23$ for glass and $h \leq 50$ for SnO₂.

Crystallinity in Ultra-thin Films:

Films with thicknesses of 150 Å, comparable to p-layer thicknesses in operational devices, were deposited and their crystallinity characterized. Two CO₂ levels of 0.33 and 0.5 were investigated with a hydrogen dilution of 50. Other deposition parameters were kept the same as before. Deposition times for these films were estimated from the deposition rates measured on thicker films deposited on SnO₂ substrates. Raman analysis of the films showed that on SnO₂ coated substrates the films had all amorphous character while on glass substrates substantial crystalline fractions were observed for both CO₂ levels. Since deposition rates on glass substrates are lower than on SnO₂, on glass substrates, the c-Si phase forms at film thicknesses considerably less than 150 Å. It can then be concluded that lack of crystallinity on SnO₂ coated substrates is not simply due to the small film thickness.

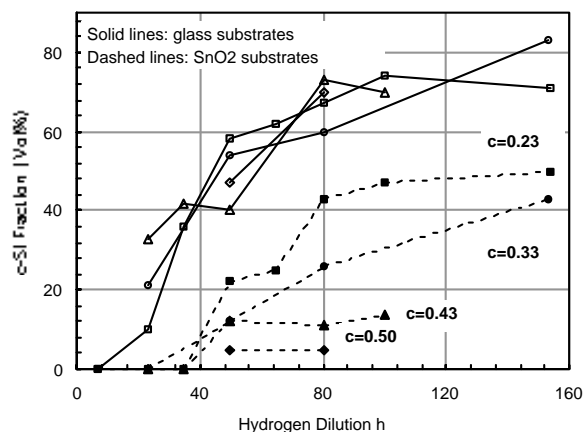


Figure 1. c-Si fraction as a function of hydrogen dilution for different levels of CO₂ in the discharge

To substantiate this observation similar films were deposited on the substrates coated in-situ with ~ 10 Å of SiO_x. Raman spectroscopic analysis of these films indicates the presence of a c-Si phase. For $c = 0.43$, numerical analysis of the data gives a c-Si volume fraction of 20% and 35% respectively for glass and SnO₂ substrates. For $c = 0.33$, the analysis gives c-Si volume fractions of 44% and 34% respectively. For both CO₂ dilutions deconvolution of the Raman data gives smaller c-Si peak width for the films deposited on glass, suggesting that SiO_x film thickness was thick enough to provide a base for c-Si nucleation but not thick enough to suppress totally the effect of the underlying substrate.

Conclusion

Two phase films of B doped c-Si imbedded in a matrix of a-SiO_x:H:C for potential use as p-layers in a-Si:H based p-i-n solar cells were deposited by RF PECVD. Structural properties of these films were characterized as a function of SiH₄, CO₂ and B₂H₆ gas flows. Compositionally, the amorphous matrix contains an order of magnitude more oxygen than carbon insuring high transparency. Low power density used for the deposition coupled with the presence of CO₂ and He buffer gas in the discharge lowers the risk of chemically reducing SnO₂, during the deposition. At film thicknesses required for the p-layers in devices, nucleation of the c-Si phase on SnO₂ requires ~ 10 Å thick SiO_x base layer which should be operationally benign in the solar cell.

Acknowledgement

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Reference

1. E. Eser, S. S. Hegedus, W. A. Buchanan, Proceedings of 15th NCPV Photovoltaics Program Review, Denver, CO (1998), p 254.